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tached thiols. This would imply that the induced alignment is affected by the intricate interactions between the pseudo SAM and the employed liquid crystal. Preliminary experiments using a polar thiol (i.e., using  $\alpha,\omega$ -mercaptohexanol), for instance, resulted in a non-uniform, predominantly planar alignment of the same liquid crystal. Depending on the density of unsaturations that are initially present on the surface of the uncured LPP material, possible interdigitation effects of the liquid crystals may also play a role if the formed pseudo SAM possesses a poor level of organization. A more detailed study of the factors involved in the alignment behavior is therefore required, such as the effect of polarity, spacer length, or cross-section diameter of the employed thiols on the pretit angle and anchoring energy of these alignment layers.

The demonstrated liquid-crystal alignment method nevertheless opens a new field for the complete and versatile control of the anchoring of liquid crystals in liquid-crystal-based devices. This is particularly important for the further improvement of the optical characteristics in these devices, and opens new possibilities for the design, manufacturing and application of completely novel display concepts.

## Experimental

**Materials:** The thiols *n*-decanethiol, *n*-hexadecanethiol, and 6-mercapto-1-hexanol were purchased from Sigma-Aldrich Chem. Co., Zwijndrecht, The Netherlands. Perfluorodecanethiol was obtained from ABCR GmbH, Karlsruhe, Germany. *n*-Dodecanethiol and the liquid crystal E7, a mixture consisting of 50.6 % 4'-pentylcyanobiphenyl, 25.2 % 4'-heptylcyanobiphenyl, 17.8 % 4'-octyloxycyanobiphenyl, and 6.4 % 4'-pentylcyanoterphenyl (GCMS), were supplied by Merck Ltd., Darmstadt, Germany. The LPP photoalignment material (Staralign 2110 CP2) was obtained from Vantico Ltd., Basel, Switzerland. The thermal initiators Trigonox C (*tert*-butyl peroxybenzoate,  $t_{1/2}$  = 10 h at 103 °C) and AIBN (2,2-azobis(isobutyronitrile),  $t_{1/2}$  = 6 min at 101 °C), were obtained from Akzo Nobel, Arnhem, The Netherlands. The photoinitiator Irgacure 651 ( $\alpha,\alpha$ -dimethoxydeoxybenzoin) was obtained from Ciba Specialty Chemicals, Basel, Switzerland. All chemicals were used without further purification.

**Substrate Design and Manufacture:** Glass substrates coated with indium tin oxide (Merck Ltd., Darmstadt, Germany) were thoroughly cleaned using a 5 vol.-% Extran MA-01 alkaline soap solution (Merck), rinsed extensively with demineralized water, washed with ethanol and subsequently dried with nitrogen. The uncured LPP material was spun (Karluss RC 8, CT 62 spincoater, 3000 rpm, 60 s) on the glass substrates, dried for 10 min at 130 °C, and subsequently allowed to gradually cool down to room temperature.

**Photoalignment and Thiol-Ene Addition:** The uncured LPP material was locally irradiated for 10 min using a medium pressure mercury UV light source (Oriol Instruments) in combination with a UV cut-off filter (Schott, WG295), a band-pass filter (Schott, UG11,  $\lambda$  = 280–320 nm, effective light intensity at sample position 7 mWcm<sup>-2</sup>), a UV linear dichroic polarizer (Oriol Instruments, model no. 27320), and an illumination mask. The partially cured LPP substrate was covered with the thiol, containing 1 wt.-% of a thermal radical initiator (Trigonox C or AIBN), using a syringe equipped with a 0.2  $\mu$ m filter. After thermal treatment at 130 °C for 30 min, the thiol-covered substrate was carefully and extensively rinsed with ethanol and dried with nitrogen. Subsequent linearly polarized or unpolarized UV-flood exposure (10 min) ensured the complete conversion of the unsaturations present in the bulk of the not yet illuminated LPP areas.

**Cell Construction:** Display cells were constructed by pairing two substrates and fixing them using a UV-curable acrylate based adhesive (Bisphenol A ethoxylate diacrylate containing 0.5 wt.-% 1-hydroxy cyclohexyl phenylketone). The cells were filled with the liquid crystal using capillary motion at elevated temperature, well above the clearing point of the mesogen. After complete filling, the cell was allowed to gradually cool down to room temperature.

**Alignment Evaluation:** Polarized optical microscopy (Axioplan 2 imaging microscope equipped with digital camera) was used to optically evaluate the anchoring characteristics of the liquid crystal.

**IR Analysis:** IR spectra of thin films were recorded using a Biorad FTIR FTS 6000 spectrometer, equipped with a Biorad UMA-500 IR microscope, at a resolution of 4 cm<sup>-1</sup>.

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## High-Performance Polymer Solar Cells of an Alternating Polyfluorene Copolymer and a Fullerene Derivative\*\*

By Mattias Svensson, Fengling Zhang, Sjoerd C. Veenstra, Wiljan J. H. Verhees, Jan C. Hummelen, Jan M. Kroon, Olle Inganäs, and Mats R. Andersson\*

The development of conjugated polymer solar cells is in an early phase, and many issues of materials and device develop-

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ment remains to be resolved. Some serious limitations for present devices are due to the relatively low mobility of charge carriers in the organic semiconductors and the narrow absorption bands.<sup>[1]</sup> The record performance of solar cells based on polymer/molecule composites today is 2.5 % under AM1.5G (100 mW cm<sup>-2</sup>).<sup>[1b,2]</sup> To go beyond this level, we need better materials and improved control over the device architecture. The latest development of new materials for polymer light-emitting diodes (PLEDs) has been concentrated to polyfluorene copolymers. This class of polymers generally exhibits high mobility and stability.<sup>[3]</sup> They normally have a liquid-crystalline state at elevated temperatures that can be used to induce higher order in the material, to give an even higher mobility and also to give polarized emission if desired.<sup>[4]</sup> Emission is typically found in the blue and green part of the visible spectrum, but by preparing different copolymers of polyfluorene, LEDs with emission spanning the whole visible spectrum have been achieved.<sup>[3a,5]</sup>

Polyfluorenes have recently been used to prepare polymer/polymer photodiodes,<sup>[6]</sup> but the devices are mainly absorbing at short wavelengths. The absorption of polyfluorene copolymers has so far been limited to relatively short wavelengths due to their large bandgap, although a few exceptions exist.<sup>[5b,c,6d,7]</sup> Our goal is to prepare efficient and stable solar cells. For use in efficient solar cells, the absorption of the active material must cover the major visible part of the solar spectrum, i.e., the bandgap should be sufficiently low. Therefore we have concentrated our efforts on the preparation of polyfluorene copolymers with relatively low bandgap, i.e., with extended absorption.

Here, we report our results on preparing an alternating polyfluorene copolymer with extended absorption, and sandwich solar cells based on the polymer and a fullerene derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester<sup>[8]</sup> (PCBM). The polymer we have prepared is poly(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole))<sup>[9]</sup> PFDTBT, (Fig. 1). Solar cells prepared from these materials indicate that PFDTBT is a very promising polymer for use in solar cells together with PCBM, due to its broad optical absorption and possibly high mobility.

The synthetic route to PFDTBT is depicted in Figure 1. The design of the polymer is based on planar conjugated segments with internal donor–acceptor functions between substituted fluorene groups. Similar polymers have been prepared and patented by Dow Chemicals, but they used maximum 50 % of the same segment as we use and at least 50 % of another small segment between the fluorene groups.<sup>[5c]</sup> They used two identical side chains on the fluorene unit whereas we are using two different side chains.<sup>[10]</sup> We are also using different procedures for preparing the monomers and the polymer. Monomer **1** was prepared by first lithiating dibromofluorene and then adding the dioxaboralane. Dibromobenzothiadiazole was coupled with two thiophene boronic acids and subsequently brominated with NBS to yield monomer **2**. The alternating copolymer PFDTBT was prepared according to a patented polymerization procedure.<sup>[11]</sup> When we prepared the

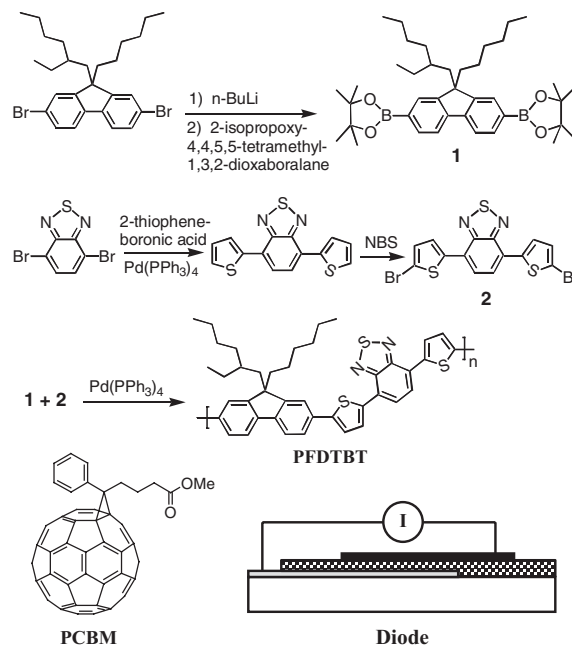


Fig. 1. Synthetic procedure for the preparation of PFDTBT, the structure of PCBM, and a simple sketch of the diode configuration.

polymer using a 1:1 ratio of the two monomers, only a small fraction of the polymeric product could be dissolved in chloroform. Upon using a 10 % excess of the fluorene monomer, to reduce the molecular weight and increase the yield, most of the prepared polymer was soluble in chloroform. The number-average molecular weight of the chloroform-soluble part, relative to polystyrene standards, as determined by size-exclusion chromatography (SEC), was  $\overline{M}_n = 4800$  and  $\overline{M}_w = 14\,000$ . This is a low molecular weight compared to other polyfluorenes prepared in the same way.<sup>[11]</sup> The limited solubility of the polymer arises from the large number of unsubstituted aromatic rings along the polymer backbone, which make chains with high molecular weight insoluble. We have also seen that the polymer is more soluble in toluene than in chloroform, but less soluble in xylene.

Films of the polymer show the longest wavelength absorption maximum at approximately 545 nm (Fig. 2a) when spin-coated from chloroform (dot-dashed line in Fig. 2a), xylene (dashed in Fig. 2a), and toluene (dotted in Fig. 2a). The films from xylene solution show small grains, and they are not as even as the films from chloroform, pointing to insolubility as a cause.

Polymer solar cells were fabricated by using PFDTBT as an electron donor and a fullerene derivative (PCBM) as an electron acceptor. We have prepared composite single-layer photodiodes (Fig. 1) by spin-coating a chloroform solution of PFDTBT and PCBM on the surface of the anodes. In all cases, we have used anodes of indium tin oxide/poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (ITO/PEDOT-PSS) and evaporated Al cathodes, with an interfacial layer of LiF.

The external quantum efficiency (EQE) of the single layer of polymer:PCBM composite (presumably a distributed het-

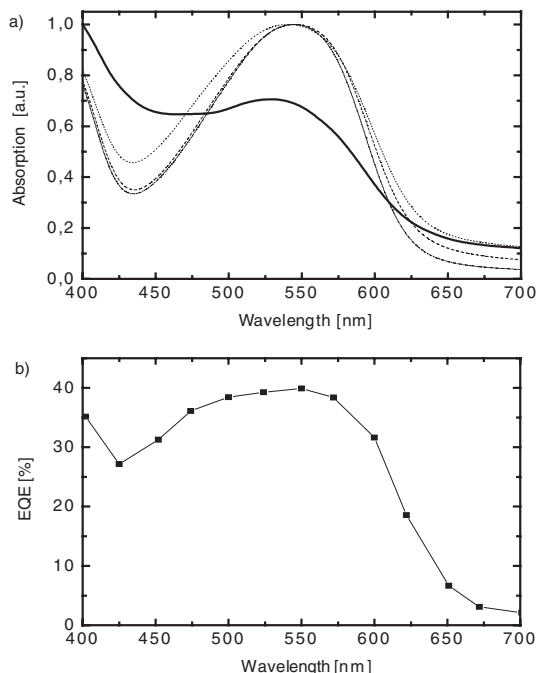


Fig. 2. a) The normalized absorption spectrum of spin-coated films of PFDTBT from chloroform (dot-dashed line), xylene (dashed line), toluene (dotted line) and the absorption of a film from a composite of PFDTBT:PCBM (1:4) spin-coated from chloroform (solid line). b) The external quantum efficiency (EQE) of a device (1.0 cm<sup>2</sup>) illuminated by monochromatic light.

erojunction device) illuminated by monochromatic light (Fig. 2b) is consistent with its broad optical absorption spectrum (solid line in Fig. 2a). The current–voltage ( $I$ – $V$ ) characteristic of a diode under simulated solar light AM1.5G (100 mW cm<sup>−2</sup>) is shown in Figure 3. The short-circuit current ( $I_{sc}$ ) is 4.66 mA cm<sup>−2</sup> and the open-circuit voltage ( $V_{oc}$ ) is 1.04 V, the fill factor (FF) is 0.46 and the energy conversion efficiency (ECE) is 2.2 % for a 1.0 cm<sup>2</sup> diode. Smaller diodes on the same substrate have similar characteristics with ECE 2.2, 2.2, and 2.4 % for areas of 0.10, 0.14, and 0.33 cm<sup>2</sup>, respectively.

The spectral coverage for photodiodes prepared from PFDTBT/PCBM (Fig. 2b) exhibit a clear red-shift compared to earlier prepared high-performance polymer solar cells of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]/PCBM (MDMO-PPV/PCBM).<sup>[1b,2]</sup> The red-shift is

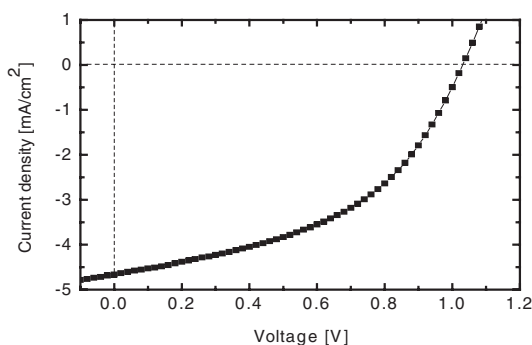


Fig. 3. The photocurrent density of the photodiode (1.0 cm<sup>2</sup>) under simulated solar light (AM 1.5G, 100 mW cm<sup>−2</sup>, 25 °C).

approximately 50 nm. This helps in generating larger photocurrents, as the photon flow is very high in this energy range. This, and the relatively high external quantum efficiency over the entire absorption band in the blend, is the main cause of the high photocurrent density obtained. The photocurrent density obtained for this cell is of the same order as for the best MDMO-PPV/PCBM cells. The maximum EQE values (0.4) are in fact lower than for MDMO-PPV/PCBM cells (EQE<sub>max</sub> = 0.5), which indicates that the improved red response leads to enhancement of the current. Despite of the red-shifted absorption, the  $V_{oc}$  is actually 0.17 V higher when compared to MDMO-PPV/PCBM (0.87 V) cells. The FF results from a complex interplay of photocurrent generation and transport through the film, and is generally expected to increase with a higher mobility of charge carriers in the composite. Whether this is the cause remains to be studied.

When comparing these results to the present day energy conversion efficiency record of 2.5 %, <sup>[2]</sup> we note that full optimization of our devices has not yet been carried out, but is underway. We also note that processing of the photoactive layer is done in normal lab atmosphere using a laminar flow box. This may negatively affect the performance of the devices. We are therefore confident that these energy conversion efficiency results can be enhanced.

In conclusion, we have prepared an alternating polyfluorene copolymer, PFDTBT, with low molecular weight and used the polymer as an electron donor in polymer solar cells. Our results indicate that PFDTBT is a promising candidate for obtaining high energy conversion efficiency when combined with a suitable electron acceptor such as PCBM. Despite the incorporation of high amounts of low-bandgap segments without solubilizing side chains in the polyfluorene copolymer, it was possible to prepare a soluble low molecular weight polymer. High-performance solar cells with extended spectral coverage and increased open-circuit voltage could be prepared from composites prepared from PCBM and the polymer. Further optimization of the processing is necessary to fully exploit the advantages of this material, as well as studies of the charge transport in the copolymer.

## Experimental

**Measurements:** NMR spectra were recorded on a Varian 400 MHz spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded using a VG ZabSpec; fast atom bombardment (FAB) was used as the ionization method. The compound to be investigated was dissolved in 3-nitrobenzyl alcohol (NBA), and a beam of Cs ions was used to ionize the sample. Molecular weights of the polymers were determined by SEC using a Waters WISP 712 equipped with three SDVB columns and a Waters 486 UV detector at 25 °C. The calibration was made with a series of monodispersed polystyrene standards in CHCl<sub>3</sub>. Flash chromatography was performed on a Jones Chromatography, Flashmaster personal. The absorption spectra of the PFDTBT and PFDTBT:PCBM films were measured using a Perkin Elmer  $\lambda$ 9 spectrophotometer. All photodiode characterization was carried out on sealed devices under a Class A solar simulator at room temperature against a calibrated GaAs reference cell, using the same procedures and set-up as described in the literature [1b].

**Synthesis:** *n*-Butyl lithium was obtained from Acros Organics. All other chemicals were purchased from Aldrich and used without further purification. 2,7-Dibromo-9-(2'-ethylhexyl)-9-hexylfluorene [10b], 4,7-dibromo-2,1,3-benzotia-

diazole [12], and 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9-(2''-ethylhexyl)-9-hexylfluorene (**1**) [13] were prepared following previously published procedures.

**4,7-Di-2'-(5'-bromo)-thienyl-2,1,3-benzothiadiazole:** To a stirred solution of 4,7-dibromo-2,1,3-benzothiadiazole (1.32 g, 4.5 mmol), and tetrakis(triphenylphosphine)-Pd(0) (95 mg, 0.09 mmol) in 1,2-dimethoxyethane (50 mL) was added 2-thiophene boronic acid (1.5 g, 11.7 mmol) and 1 M NaHCO<sub>3</sub> (40 mL). The mixture was refluxed overnight and 1,2-dimethoxyethane was evaporated under vacuum. The product was extracted with diethyl ether, successively washed with 1 M NaOH and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent afforded the crude product as a red oil that was further purified using flash chromatography (silica gel, petroleum ether 40–60 °C/ethyl acetate, 50:1 as eluent) to yield 1.15 g (85 %) of the product as red crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ [ppm] 6.61 (d, 2H), 7.21 (t, 2H), 7.43 (d, 2H), 7.84 (s, 2H). High-resolution mass spectrometry (HRMS): Calcd for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>3</sub>: 299.985. Found: 299.986.

**4,7-Di-2'-(5'-bromo)-thienyl-2,1,3-benzothiadiazole (**2**):** To a stirred solution of 4,7-di-2'-thienyl-2,1,3-benzothiadiazole (1.44 g, 4.8 mmol) in dimethylformamide (DMF) (25 mL), was added NBS (2.05 g, 11.5 mmol) in darkness. The mixture was stirred at room temperature for 16 h and 2 M HCl was added. The product was extracted into chloroform and the organic phase was washed with 10 % sodium bisulfite, 2 M HCl and water successively and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed to afford the product as dark red crystals that were recrystallized from chloroform to afford 1.30 g, (59 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ [ppm] 7.13 (d, 2H), 7.80 (dd, 4H). HRMS: Calcd for C<sub>14</sub>H<sub>6</sub>N<sub>2</sub>S<sub>3</sub>Br<sub>2</sub>: 455.806. Found: 455.809.

**Poly(2,7-(9-(2'-ethylhexyl)-9-hexylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)) (PFDTBT):** 4,7-Di-2'-(5'-bromo)-thienyl-2,1,3-benzothiadiazole (0.15 g, 0.33 mmol) was mixed with 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9-(2''-ethylhexyl)-9-hexylfluorene (0.22 g, 0.36 mmol, 1.1 equiv), tetrakis(triphenylphosphine)Pd(0) (3.0 mg, 2.6 μmol) and toluene (6 mL) and refluxed for 10 min under N<sub>2</sub>. Tetraethylammonium hydroxide (1.0 mL, 20 wt.-% in water, 1.4 mmol) was added with a syringe and the mixture was refluxed for 2.5 h. Bromobenzene (0.05 g, 0.32 mmol) was added and after 1 h reflux phenylboronic acid (0.06 g, 0.5 mmol) was added. After 1 h reflux the polymer was precipitated in MeOH and filtered off. The polymer was dissolved in CHCl<sub>3</sub> and conc. NH<sub>4</sub>OH was added. After stirring overnight the phases were separated and the organic phase was washed with water, filtered and evaporated until 5 mL remained. The polymer was precipitated in methanol and filtered off to yield 0.147 g (approx. 60 %) of the pure polymer. <sup>1</sup>H NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ [ppm], 0.5–1.5 (m, 26H), 2.13 (b, 4H), 7.49 (b, 2H), 7.72 (b, 6H), 7.94 (b, 2H), 8.22 (b, 2H).

**Device Preparation:** For all devices, the basic geometry is a thin layer of the conducting polymer complex of PEDOT-PSS (EL grade, Bayer AG) as polymer anode. This layer was deposited by spin-coating on a UV-ozone-treated ITO-coated glass substrate, followed by annealing at 120 °C for 5 min, to facilitate the hole collection. The composite single-layer diodes were built by spin-coating solutions with PFDTBT and PCBM (weight ratio 1:4) in chloroform (30 mg mL<sup>-1</sup>). The polymer layer thickness was between 100–200 nm, depending on coating conditions. Deposition of the PEDOT and PFDTBT:PCBM was carried out in an ambient atmosphere using a laminar flow box. The substrates were transferred to a glove box and a thin lithium fluoride (LiF) (1.0 nm) layer was deposited on top of the composite film. Subsequently, an Al (60 nm) cathode was deposited on top of the LiF layer, after which the diodes were sealed inside the glove box. The size of the active area of the diodes prepared on the same substrate was 0.10, 0.14, 0.33, and 1.0 cm<sup>2</sup>.

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Note added in proof: Recently two publications presenting poly(3-hexylthiophene):PCBM solar cells with ECE results in the range of 3 % have been published.<sup>[14]</sup>

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## Formation of Polarization Gratings and Surface Relief Gratings in Photocrosslinkable Polymer Liquid Crystals by Polarization Holography\*\*

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As a result of the myriad of potential applications such as optical memory devices, thin film optical filters, and integrated optical devices, photoinduced orientation in photosensitive polymer systems has received a great deal of attention.<sup>[1,2]</sup> One area well researched is holographic diffractive elements, and several types of photosensitive materials have been developed into new holographic grating devices, including photochromic polymers<sup>[3–6]</sup> and photoreactive polymers.<sup>[7,8]</sup> Numerous studies reported that irradiating polymers containing azobenzene side groups with linearly polarized

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